

Benchmarking DFT functionals for excited-state calculations of Donor Acceptor TADF emitters: Insights on the key parameters determining Reverse Inter System Crossing

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Abstract

The importance of intermediate triplet states and the nature of excited states has gained interest in recent years for the thermally activated delayed fluorescence (TADF) mechanism. It is widely accepted that simple conversion between charge transfer (CT) triplet and singlet excited states is too crude, and a more complex route involving higher-lying locally excited triplet excited states has to be invoked to witness the magnitude of the rate of reverse intersystem crossing (RISC) rates. The increased complexity has challenged the reliability of computational

methods to accurately predict the relative energy between excited states as well as their nature. Here we compare the results of widely used DFT functionals, CAM-B3LYP, LC- ω PBE, LC- ω^* PBE, LC- ω^* HPBE, B3LYP, PBE0 and M06-2X against a wavefunction-based reference method, Spin-Component Scaling second-order approximate Coupled-Cluster (SCS-CC2) in fourteen known TADF emitters possessing a diversity of chemical structures. Overall, the use of the Tamm-Dancoff Approximation (TDA) together with the CAM-B3LYP, M06-2X and the two ω -tuned range-separated functionals LC- ω^* PBE and LC- ω^* HPBE demonstrated the best agreement with SCS-CC2 calculations in predicting the absolute energy of the singlet S_1 , and triplet T_1 and T_2 excited states and their energy differences. However, consistently across the series and irrespective of the functional or the use of TDA, the nature of T_1 and T_2 is not as accurately captured as compared to S_1 . We also investigated the impact of the optimization of S_1 and T_1 excited on ΔE_{ST} and the nature of these states for three different functionals (PBE0, CAM-B3LYP and M06-2X). We observed large changes in ΔE_{ST} using CAM-B3LYP and PBE0 functionals associated with a large stabilization of T_1 with CAM-B3LYP and a large stabilization of S_1 with PBE0 while ΔE_{ST} is much less affected considering M06-2X functional. The nature of the S_1 state barely evolves after geometry optimization essentially because this state is CT by nature for the three functionals tested. However, the prediction of the T_1 nature is more problematic since these functionals for some compounds interpret the nature of T_1 very differently. SCS-CC2 calculations on top of the TDA-DFT optimized geometries leads to a large variations in terms of ΔE_{ST} and the excited state nature depending on the chosen functionals further stressing the large dependence of the excited states features on the excited states geometries. The presented work highlights that despite good agreement of energies, the description of the exact nature of the triplet states should be undertaken with caution.

1) Introduction

Research focusing on materials that display thermally activated delayed fluorescence (TADF) has become very important in recent years due largely to their strong potential as emitters in electroluminescent devices, as imaging reagents in biological systems and as photocatalysts.¹⁻⁴ Although the photophysical concept of TADF has been known for decades,⁵⁻⁸ it has only recently been recognized as a triplet harvesting pathway in organic light-emitting diodes (OLEDs).⁹⁻¹⁰ Spin statistics dictate that upon charge injection from the anode and the cathode, the recombination of a hole and an electron, excitons will form in a 3:1 ratio of triplets to singlets.² Through TADF, an Internal Quantum Efficiency (IQE) of up to 100% is possible, matching the IQE of phosphorescent OLEDs.

In the TADF mechanism, the normally non-emissive triplet excitons are converted to emissive singlet through an endothermic reverse intersystem crossing (RISC). Intersystem crossing (ISC) and RISC are formally spin-forbidden processes and are only possible when there is mixing of the S₁ to T₁ wavefunctions, which can be quantified in terms of the first-order mixing coefficient, λ , (equation 1).¹¹ This term is itself dependent on the degree of SOC between the singlet and triplet states and the energy difference between them, ΔE_{ST} (Eq. 1),

$$\lambda = \frac{SOC}{\Delta E_{ST}} \quad (1)$$

SOC itself can only occur when the orbital type of the singlet and triplet states are distinct, thereby satisfying El Sayed's rules.¹² In D-A TADF materials, SOC between CT states of different spin multiplicities is forbidden while SOC between a CT state and a locally excited states (LE) is large (Figure 1). SOC is proportional to Z^4 (where Z is the atomic number) of the atoms involved in the transitions to S₁ and T₁.¹³ This is the origin of the very fast ISC rates in phosphorescent metal complexes (usually iridium) and is coined the heavy atom effect. However, SOC is expected to be low in TADF emitters which are composed primarily of 1st and 2nd row elements. Decrease in ΔE_{ST} is facilitated by decoupling of the hole and the electron

densities associated with T_1 and S_1 states, which occurs in CT states as opposed to LE states, which have strongly overlapping ground and excited state densities (Figure 1b).

Equation 1 characterizes the degree of state mixing between T_1 and S_1 , which should be large to trigger efficient direct RISC from T_1 to S_1 . However, a direct conversion from T_1 to S_1 is not necessarily the most efficient conversion path when the nature of T_1 and S_1 are largely similar as this results in a very small SOC. A spin vibronic mechanism can be invoked, where vibronic coupling between T_1 and higher lying triplet states (T_n) occurs, permitting reverse internal conversion (RIC) prior to RISC from the higher-lying T_n state.¹⁴ When the higher-lying triplet state is of different orbital type to S_1 (i.e., LE) then El Sayed's rules are satisfied, leading to non-negligible SOC and a large degree state mixing. Indeed, this mechanism is frequently invoked in the literature to explain fast k_{RISC} rates despite the moderately large ΔE_{ST} . Quantum chemical calculations are frequently employed to rationalize such a mechanism by computing the higher-lying triplet excited states where spectral assignment is rather challenging.¹⁵⁻¹⁹

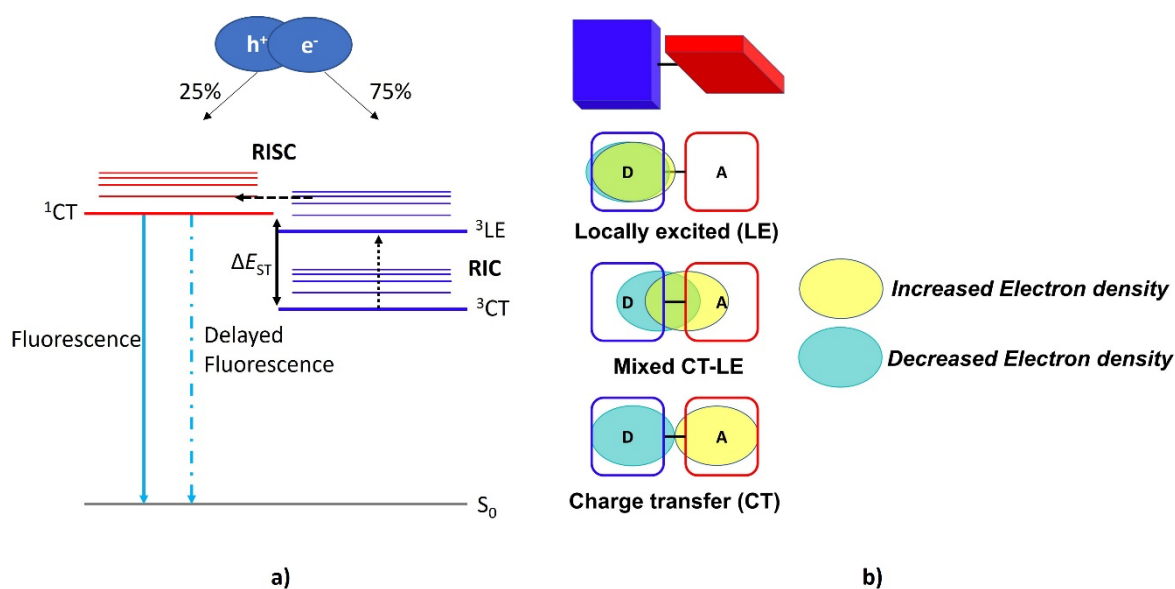


Figure 1. a) Simplified Jablonski diagram showing a TADF mechanism involving spin-vibronic coupling to intermediate triplet states, where h^+ is hole, e^- is electron, with $h^+ : e^-$ the corresponding electron:hole pair created, RISC is reverse intersystem crossing and RIC is

reverse internal conversion; **b**) simplified picture of the electronic density distribution of different electronic excited states in a D-A prototypical molecule.

The picture presented in the literature largely supports the existence of pure CT and LE states. Recently, using a combination of molecular dynamics (MD) and excited state calculations using Time-Dependent Density Functional (TD-DFT) within the Tamm-Dancoff approximation (TDA-DFT), some of us demonstrated that the nature of the excited states is often more complex.²⁰ That work highlighted that excited states are actually mixed between CT and LE, and the degree of mixing is dynamically modulated by the fluctuations of the dihedral angles between the electron donating and accepting units. This is corroborated by a four-state model, which demonstrated that the electronic coupling of the diabatic states (purely CT and LE states) at the off-equilibrium geometries induces sufficiently different character between the adiabatic S_1 and T_1 states, so a direct rISC is possible without invoking the effective population of a higher-lying triplet state.²⁰⁻²³

The design of TADF emitters has been largely assisted by excited state calculations at the TD-DFT level,²⁴ either in its full treatment or using TDA-DFT.²⁵ The use of the latter is now quite well established as a potential solution to addressing the known triplet instability issue inherent in TD-DFT calculations.²⁶⁻²⁸ High-throughput screening, particularly in industry, has been adopted as a rapid TADF discovery tool.²⁹⁻³⁰ The screening is often based on the optimization of ΔE_{ST} in tandem with the oscillator strength. However, this approach only focused on the lower-lying excited states and did not investigate the potential presence of closely-lying triplet excited states, which could assist RISC.

The most common functionals used within the TADF community are hybrid ones that have a low or moderate content of Hartree-Fock like exchange (% HF), such as B3LYP³¹ (20% HF) and PBE0³² (25% HF). The use of these functionals in conjunction with modest-sized basis

sets such as 6-31G* typically provide a satisfactory agreement of both the excited state energies and ΔE_{ST} with the experiment.²⁶ However, it is important to understand that the calculations do not model either the fluorescence or phosphorescence transitions but rather vertical absorption processes are simulated based on an optimized ground state geometry. Further, nearly all calculations reported in the TADF literature are gas-phase calculations and thus do not take into account the effects of the polarity of the medium, which will more strongly influence the energy of CT states. Long-range functionals such as ω B97XD³³⁻³⁴ and LC- ω PBE³⁵ were developed to improve the description of CT excited states and have initially appeared as alternatives to the previous family of functionals in an effort to more accurately and consistently describe the low-lying CT states present in TADF materials. However, generally, larger ΔE_{ST} are predicted likely because S_1 and T_1 possess a larger LE character as compared to PBE0 and B3LYP calculations, resulting in a poorer agreement with the experimental data.^{20, 28} A greater degree of accuracy is possible using LC- ω PBE and ω B97XD, where the range-separation parameter, ω , representing the inverse of the distance at which the exchange term switches from DFT-like to HF like, is optimized for every system (and potentially for every conformation³⁶). Adopting this methodology dramatically increases the computational cost for modelling the TADF materials since these functionals become compound and geometry specific. While hybrid functionals, including those containing a low percentage of the Hartree-Fock like exchange, are known to underestimate excited state energies of CT excited states,²⁸ functionals with higher HF like contributions like the meta-GGA hybrid functionals from the Minnesota family (e.g., 54% for M06-2X) have emerged to address this weakness,³⁷ without the need to explicitly tune parameters.

Moving beyond DFT calculations, coupled cluster-based methods are considered as some of the most accurate for calculating the properties of ground and excited states of molecules.³⁸ In particular, the spin-component scaling second-order approximate coupled-cluster (SCS-CC2)³⁹

calculations used together with the resolution-of-the-identity, have appeared as a cost-effective method to treat molecular systems up to a hundred atoms. SCS-CC2 differs from CC2 by the introduction of different scaling factors for the same-spin and opposite-spin contributions to the correlation energy. SCS-CC2 calculations provide a very high level of accuracy in the predictions of both singlet and triplet energies and ΔE_{ST} , and has been used to great effect when modelling singlet fission⁴⁰ and multi-resonant TADF (MR-TADF) materials.⁴¹ SCS-CC2 is not, however, an affordable method for the high-throughput screening of new emitters,²⁹⁻³⁰ for larger systems, or for excited state calculations performed on geometries extracted along a MD trajectory.^{20, 42-43}

Using TD(A)-DFT approaches, several benchmarking studies have been reported with the goal of identifying the most appropriate functionals to use in terms of providing accurate predictions with experiment. Based on a set of six compounds, Moral *et al.*²⁶ showed that the use of TDA-DFT led to a more accurate prediction of ΔE_{ST} , compared to TD-DFT. Using a larger set of seventeen molecules that possess a wide range of experimental ΔE_{ST} values, Sun *et al.*²⁸ demonstrated that PBE0, M06-2X as well as ω -tuned range-separated functionals such as LC- ω PBE offered excellent agreement between experimental and computed ΔE_{ST} . A recent study by Kunze *et al.* covering twenty-seven TADF emitters across a range of structural classes⁴⁴ demonstrated how the use of spin-unrestricted and restricted open-shell Kohn–Sham self-consistent field calculations in combination with a polarizable-continuum can be used to compute with very high accuracy the adiabatic ΔE_{ST} (MAD of 0.025 eV). Each of these previous studies compared experimental ΔE_{ST} with the calculated values, and only considered S_1 and T_1 to evaluate the efficiency of the TADF process. A recent study by Cardeynaels *et al.*⁴⁵ probed the modelling of intermediate triplet states of ten D-A emitters by DFT methods and comparing the results to CC2 calculations. This study revealed that M06-2X provided the smallest MAD of 0.13 eV for the absolute energy of T_2 . Beyond this one report, the comparison

between the energies of higher lying triplet states computed at the TD(A)-DFT and a wavefunction-based methodology has not been undertaken.

Previous theoretical studies have shown that both ΔE_{ST} and SOC are in large part governed by the nature of the lowest-lying excited states.⁴⁶ The largest k_{RISC} values reported to date have been rationalized using TD-DFT analysis to involve higher-lying triplet states (Figure 2).^{15-16,}

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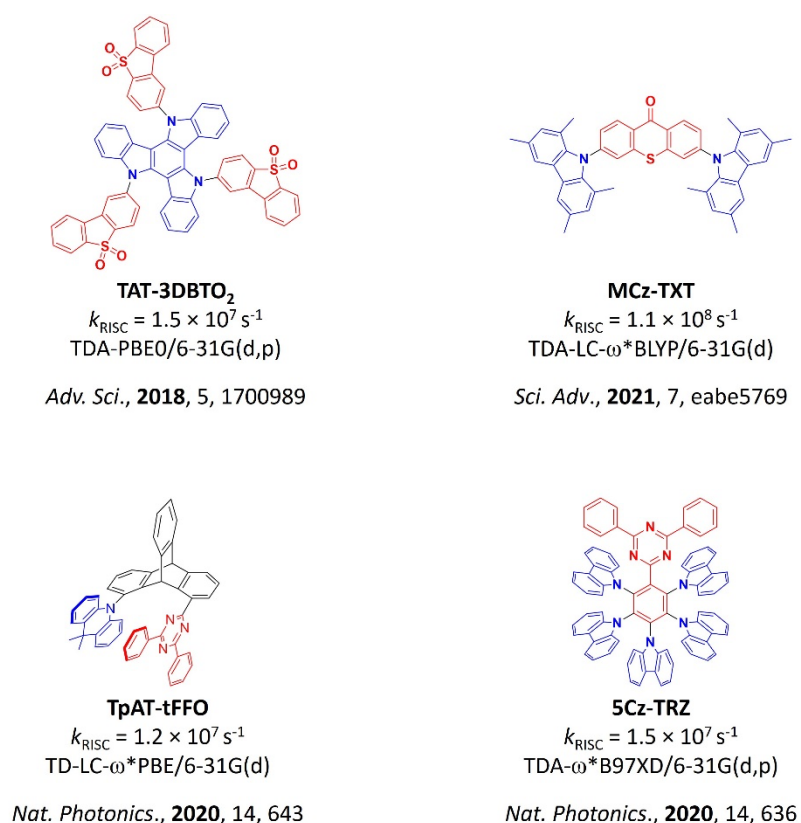


Figure 2. Structures, experimental k_{RISC} values and DFT method employed to compute the T_1 and S_1 excited states energies for TADF in these literature-reported emitters.

In the literature, several indices have been developed to quantify the degree of CT in the excited state.⁴⁷ The most popular ones rely on the charge transferred (q_{CT}) upon excitation, the distance between the hole and electron centroids (Δr), and the overlap between the hole and electron

densities based on the attachment-detachment formalism (ϕ_s).⁴⁷ We note here that relying only on a single pair of canonical orbitals to describe the transition to the excited state, and hence these indices, is problematic as the nature of the excited state frequently involves a more complex family of orbital pairs. These indices are better estimated within the Natural Transition Orbital (NTO) and the attachment-detachment formalisms⁴⁸⁻⁴⁹ or directly from an analysis of the difference density⁵⁰ between the ground and excited state, which consider the overall electronic density and not simply the canonical molecular orbitals. We note that the ϕ_s metric performs similarly to the λ metric reported earlier by Peach et al. when it was used in conjunction with the NTOs associated with a given excited state.⁵¹

In this study, we have calculated key photophysical properties of fourteen structurally diverse TADF emitters using a range of DFT functionals: B3LYP, PBE0, M06-2X, LC- ω PBE, LC- ω^* PBE, LC- ω^* HPBE and CAM-B3LYP. We cross-compared the predictions from these calculations to those using SCS-CC2 in order to determine the optimal DFT methodology for the modelling of donor-acceptor TADF emitters.

2.1 Methodology

The quoted excited states energies were primarily obtained from vertical excitations based on the optimized ground state geometry. All calculations were carried out in the gas-phase. Notably, there is a diversity of conditions, media and methods used to experimentally determine ΔE_{ST} , which introduces a certain degree of variability in the values reported. Compounds were optimized using the following DFT functionals: PBE0;³² CAM-B3LYP;⁵² B3LYP;³¹ LC- ω PBE;³⁵ ω -tuned LC- ω PBE²⁸ (LC- ω^* PBE); ω -tuned LC- ω HPBE⁵³ (LC- ω^* HPBE); and M06-2X.³⁷ Each of these functionals was used in conjunction with the D3(BJ)⁵⁴ dispersion correction scheme and the 6-31G(d,p)⁵⁵ basis set. This basis set is widely employed in TD-DFT studies and thus also in the TADF literature. Following the initial ground state

optimization, vertical excitations were calculated using both TD-DFT and TDA-DFT approaches. Additionally, for each compound, both the ground state geometry optimization and the vertical excitations were calculated at the SCS-CC2⁵⁶⁻⁵⁸ level with the cc-pVDZ⁵⁹ basis set. The choice of this Dunning basis set is appropriate for wavefunction-based approaches and keeps the computational cost relatively low.⁶⁰ Although cc-pVDZ is relatively small, previous work has highlighted that this basis performs similarly to larger basis sets such as def2-TZVP.⁴¹ The energies and nature of S₁, T₁ as well as T₂ were calculated using both TD(A)-DFT and SCS-CC2. In addition, for a subset of compounds, we also performed TDA-DFT S₁ and T₁ excited states optimization (see section 5). TD(A)-DFT calculations were performed using Gaussian 09,⁶¹ or Gaussian 16⁶² when the LC- ω *HPBE was considered, while SCS-CC2 calculations were performed using Turbomole 7.4 package.⁶³

In both LC- ω *PBE and LC- ω *HPBE methods, the range separation parameter, ω , was optimized in order to minimize the error J^2 , defined as:

$$J^2 = \sum_{i=0}^1 [\varepsilon_H(N+i) + IP(N+i)]^2 \quad (2)$$

where $\varepsilon_H(N+i)$ and $IP(N+i)$ are the HOMO energy and the ionization potential of a N-electron system (i.e., the ground state) and N+1-electron system (i.e., the radical anion). The vertical electron affinity is assumed to be equivalent to the ionization potential of the N+1-electron system. Such an approach offers a quite accurate estimate of the S₁ excitation energy and the ΔE_{ST} at the expense of the optimization of the ω parameter.

As the TADF process depends on the energy difference between excited states and not on their absolute value, we placed a particular emphasis on the comparison of the differences in energy, between S₁ and T₁ (ΔE_{ST}), between S₁ and T₂ (ΔE_{S1T2}) and between T₁ and T₂ (ΔE_{T1T2}). We note that in some cases, more than one intermediate triplet state is present between T₁ and S₁;

however, these are not explicitly accounted for in this study. We note that the greater density of intermediate triplet excited states should lead to an enhancement of the RISC rate.⁶⁴⁻⁶⁵

The nature of the excited states at the TD(A)-DFT level was determined by analysis of the ϕ_s index, which refers to the overlap between the attachment (ρ_A) and detachment (ρ_D) densities that are associated with the hole and electron densities, respectively. ϕ_s varies between 0, where there is no overlap between the hole and electron densities and indicates that the excitation is CT, and 1, where there is complete overlap of the hole and electron densities and indicates that the excitation is LE (Figure 3).⁴⁷ Values between the two represent excitations bearing a mixed CT-LE character. The ϕ_s values were obtained through a post-analysis of Gaussian outputs with the NANCY-EX 2.0 software.⁶⁶⁻⁶⁷ In the analysis of the SCS-CC2 wavefunctions, we rely on the difference density, $\Delta\rho$, computed as the difference between the excited state, ρ_{EX} , and the ground state, ρ_{GS} , densities, to characterize the nature of the excited states.

At the TD(A)-DFT level, the difference density $\Delta\rho$ is readily obtained by computing the difference $\Delta\rho$ between the attachment ρ_A and the detachment ρ_D densities.⁴⁸

Using $\Delta\rho$, several metrics to study the CT character of excited states have been investigated using the Multiwfn 3.6 software.⁶⁸ Following the work by Le Bahers *et al.*, two functions, ρ_+ and ρ_- , are defined to account for the increase and decrease in density upon electronic excitation, which reflect ρ_{EX} and ρ_{GS} , respectively.⁶⁹ The calculation of these metrics based on $\Delta\rho$, computed either at the TD(A)-DFT and SCS-CC2 levels, allow for a straightforward comparison between the two approaches. To facilitate the comparison between TD(A)-DFT and SCS-CC2, we compared the single electron difference density obtained at the SCS-CC2 level, omitting the second-order contribution.

The first metric, D_{CT} , is defined as the distance between the barycentres, R_+ and R_- , of the two density components, $\rho_+(r)$ and $\rho_-(r)$, characterizing an increase or a decrease of the electronic density at point r of space, respectively.^{50, 70} The larger D_{CT} the greater the CT character of the

excited state; however, problems can arise in centrally symmetric systems, where the calculation of the barycentre associated with a given excitation suggests a state of LE character, leading to a zero value for D_{CT} while the other indices (ϕ_s , q_{CT} , *vide infra.*) imply a state of a CT character.^{47, 50} Thus, it is advisable to employ another descriptor. The charge transferred (in number of electrons), q_{CT} , relates to the integration of ρ_+ (or ρ_-), over all space. The larger the number, the greater the extent of electronic rearrangement. A value of 0 signifies a state that is pure LE while a value of 1 is associated with a purely CT state.⁶⁹

The final metrics employed is the overlap (S_{+-}) between centroids of charges associated with positive (C_+) and negative (C_-) density, with C_+ and C_- defined as:

$$C_+(r) = A_+ e \left(-\frac{(x-x_+)^2}{2\sigma^2_{+x}} - \frac{(y-y_+)^2}{2\sigma^2_{+y}} - \frac{(z-z_+)^2}{2\sigma^2_{+z}} \right) \quad (3)$$

$$C_-(r) = A_- e \left(-\frac{(x-x_-)^2}{2\sigma^2_{-x}} - \frac{(y-y_-)^2}{2\sigma^2_{-y}} - \frac{(z-z_-)^2}{2\sigma^2_{-z}} \right) \quad (4)$$

Where A_+ and A_- are the normalization factors chosen to impose the integrated charge on the centroid to be equal to the corresponding density change integrated in the whole space. The overlap between these two points C_+ and C_- provides S_{+-} . A value equal to 1 indicates C_+ and C_- completely overlap, while a value of 0 indicates they are completely disconnected, corresponding to LE and CT electronic transitions respectively (Figure 3).

In this study, we will cross-compare the three metrics calculated from $\Delta\rho$ using SCS-CC2 and the DFT method using each of the aforementioned functionals.

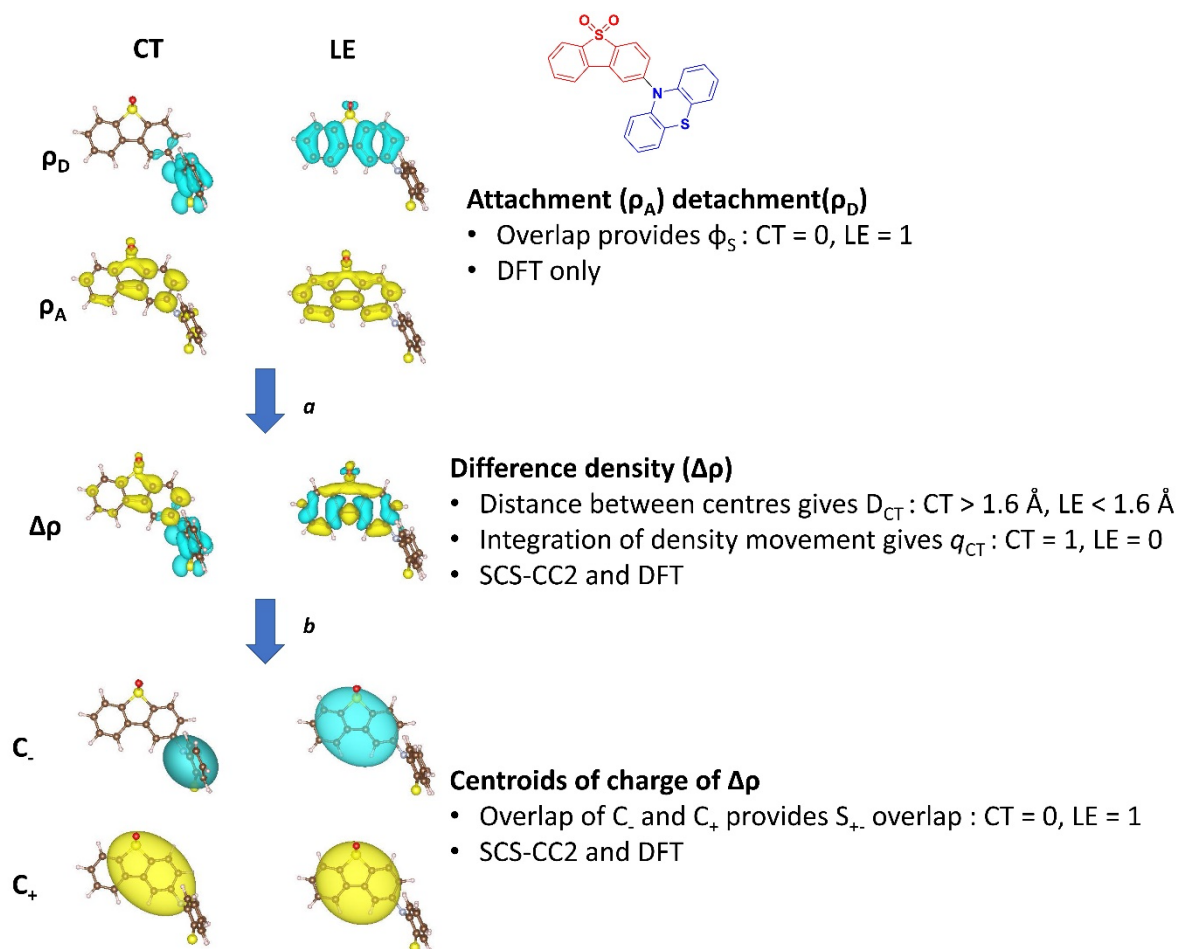


Figure 3. Pictures of the electronic density associated with a given excited state and the corresponding metrics to quantify the degree of CT for a representative donor-acceptor TADF compound, **PTZ-DBTO2** using each of the different methods (see text). Each density was calculated using TDA-CAM-B3LYP/6-31G(d,p).

To assess the predictive accuracy of each DFT functional against SCS-CC2, we report on the mean average deviation (MAD), root mean square deviation (RMSD) and standard deviation (σ) for S_1 , T_1 , T_2 , ΔE_{ST} , ΔE_{S1T2} , ΔE_{T1T2} , q_{CT} , D_{CT} and S_{+-} for each of the fourteen compounds. These are computed following the definitions in equations 6-8:

$$MAD = \frac{1}{n} \sum_{i=1}^n |x_i| \quad (6)$$

$$RMSD = \sqrt{\frac{1}{n} \sum_{i=1}^n |x_i|^2} \quad (7)$$

$$\sigma = \sqrt{\left(\frac{1}{n} \sum_{i=1}^n |x_i|^2\right) - \left(\frac{1}{n} \sum_{i=1}^n |x_i|\right)^2} \quad (8)$$

where $x_i = y_i^{DFT} - y_i^{SCS-CC2}$, y_i^{DFT} being S_1 , T_1 , T_2 , ΔE_{ST} , ΔE_{S1T2} , ΔE_{T1T2} , q_{CT} , D_{CT} or S_+ calculated at the TD(A)-DFT level and $y_i^{SCS-CC2}$ the corresponding SCS-CC2 energy, energy difference or nature, with the i index running over the series of $n=14$ studied molecules.⁷¹

2.2 Emitters in the study

The fourteen structurally diverse emitters are representative TADF compounds that show a range of photophysical behaviour (e.g., ΔE_{ST} ranging from 0.01 eV and 0.22 eV). The chemical structures are shown in Figure 4, and the photophysical properties and OLED performance are collated in Table S1.

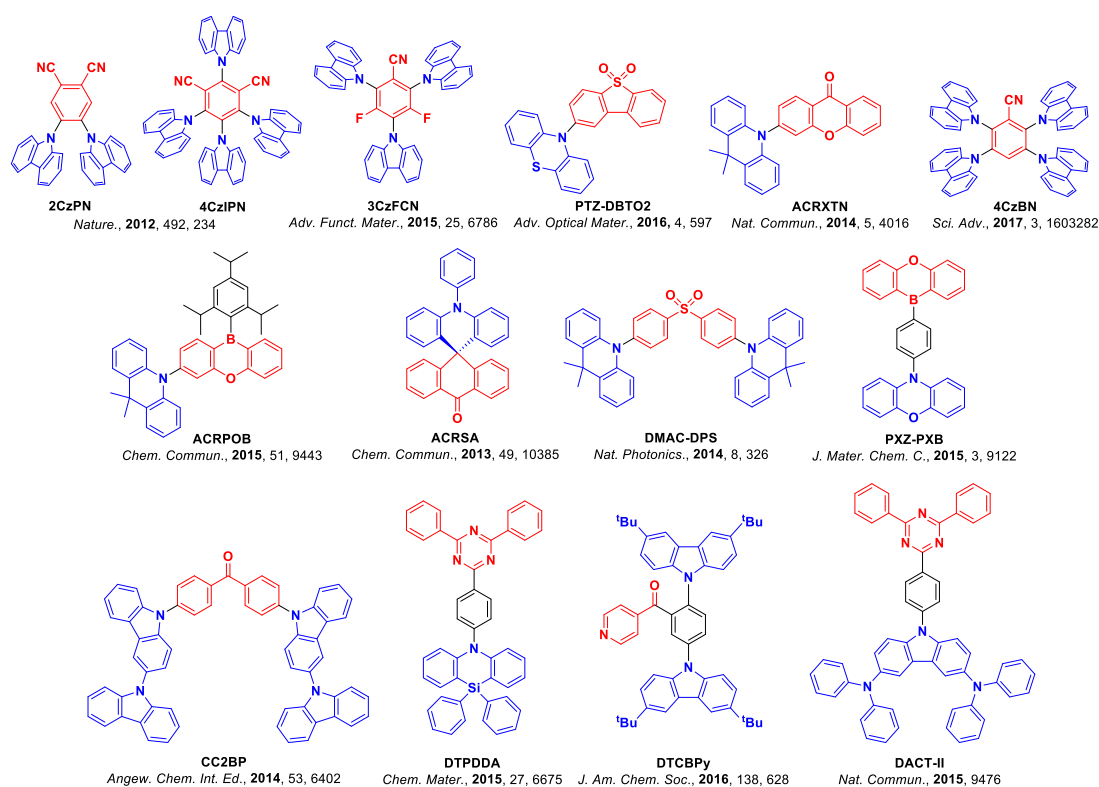


Figure 4. Chemical structures of the TADF emitters in this study. Blue components represent donor units and red components represent acceptor units.

3. Discussion and Results

3.1. Excited-state energies

We started by investigating the energies of S_1 , T_1 and T_2 (Figure S1 – S4, Tables S2 – S15). There is an evident and consistent underestimation of the excited states energies for B3LYP and PBE0 with both TD-DFT and TDA-DFT compared to SCS-CC2. This is due to the over stabilisation of CT states, which has been widely reported,⁴⁷ and mainly arises from self-interaction errors due to a low content of HF like exchange which is evident in the large MAD values (Table 1) for S_1 , T_1 and T_2 . For both B3LYP and PBE0 a slightly improved MAD is achieved for both triplet states using TDA-DFT compared with TD-DFT, which is due to an improved triplet character description. The S_1 state is predicted with a similar level of accuracy using either TD-DFT or TDA-DFT. Indeed, TD-DFT and TDA-DFT are formally equivalent when the excited states bear a strong CT character as usually observed for the S_1 state of D-A TADF materials. A smaller standard deviation is thus reported for both T_1 and T_2 than for S_1 because the exchange interaction tends to increase the LE character (decrease the CT character) of these latter states in comparison to S_1 . This is further stressing the systematic excited states overstabilization of excited states energies with strong CT obtained with low HF exchange functionals. The use of M06-2X results in vastly improved excited state energy prediction for T_1 , T_2 and S_1 , with a reduced MAD for each compound compared to SCS-CC2 (Table 1). This is due to the increased HF like contribution in this functional, which improves the description of CT excited states. Excellent agreement for both T_1 and T_2 is obtained for TDA-DFT calculations using LC- ω PBE without tuning ω , while TD-DFT calculations using the same functional largely underestimate the T_1 energies. This is likely due to the more accurate description of states with significant LE character using this functional while states with significant CT character are not well described. The ω -tuned LC- ω *PBE (LC- ω *HPBE)

functionals partially address the issue observed with LC- ω PBE, leading to a decrease in T_1 and T_2 MADs, especially at the TDA-DFT level (see Table 1). The MAD for S_1 is very similar for both LC- ω *PBE and LC- ω *HPBE using either TD-DFT or TDA-DFT. The use of TDA-CAM-B3LYP results in a closer agreement with SCS-CC2 than with TD-CAM-B3LYP, which essentially comes from an improved description of LE-dominated triplet states. The S_1 energy is also well predicted with CAM-B3LYP as this functional has been designed to more accurately describe CT states. Based on this analysis, it is clear that TDA-DFT calculations are more accurate than TD-DFT calculations, in agreement with previous findings.^{26,28} Both M06-2X and CAM-B3LYP calculations produce the smallest MAD and smallest standard deviation to the SCS-CC2 results. The summary of MAD, RMSD and σ are found in Table 1, Figure 5 and Figure S5.

Table 1. MAD, RMSD and σ on the energies of the investigated excited states in comparison to SCS-CC2.

	S_1 / eV			T_1 / eV			T_2 / eV		
	MAD	RMSD	σ	MAD	RMSD	σ	MAD	RMSD	σ
TD - CAM-B3LYP	0.10	0.12	0.06	0.46	0.46	0.07	0.47	0.50	0.15
TDA - CAM-B3LYP	0.10	0.13	0.08	0.12	0.14	0.08	0.15	0.17	0.08
TD - LC-ωPBE	0.56	0.61	0.25	0.76	0.77	0.09	0.82	0.83	0.16
TDA - LC-ωPBE	0.61	0.67	0.26	0.09	0.11	0.06	0.13	0.17	0.10
TD - LC-ω*PBE	0.45	0.47	0.14	0.52	0.53	0.10	0.56	0.57	0.10
TDA - LC-ω*PBE	0.43	0.46	0.14	0.46	0.48	0.14	0.48	0.49	0.11
TD - LC-ω*HPBE	0.45	0.47	0.13	0.52	0.53	0.10	0.56	0.57	0.10
TDA - LC-ω*HPBE	0.44	0.46	0.14	0.46	0.48	0.14	0.48	0.49	0.11
TD - B3LYP	1.03	1.06	0.24	0.89	0.91	0.18	0.80	0.81	0.14
TDA - B3LYP	1.03	1.06	0.23	0.89	0.90	0.17	0.76	0.78	0.17
TD - PBE0	0.85	0.88	0.21	0.77	0.78	0.12	0.74	0.74	0.11
TDA - PBE0	0.84	0.87	0.21	0.72	0.74	0.15	0.63	0.65	0.13

TD - M06-2X	0.15	0.18	0.10	0.15	0.19	0.12	0.18	0.20	0.08
TDA - M06-2X	0.12	0.14	0.07	0.12	0.16	0.11	0.12	0.14	0.08

3.2. Relative Energy Differences

We now turn to the prediction of the energy differences between excited states, values that are relevant when ascertaining k_{RISC} . Despite the large overstabilization of the excited state energies computed with PBE0 and B3LYP at both TD-DFT and TDA-DFT, the MADs for ΔE_{ST} are small, see Table 2. This is due to the large but similar errors computed for T_1 and S_1 . However, the MADs for ΔE_{S1T2} and ΔE_{T1T2} and their associated standard deviations are much larger than for the other functionals (Table 2). Specifically, in five examples (**PXZ-PXB**, **PTZ-DB2OT**, **DTPDDA**, **DTCBPy** and **DACT-II**) T_2 is predicted to be higher in energy than S_1 using DFT methods while this is not observed with SCS-CC2. Each of these five compounds displays S_1 and T_1 states that have large CT character, both of which are stabilized compared to other low-lying excited states (*vide infra*). ΔE_{ST} , ΔE_{S1T2} and ΔE_{T2T1} computed with M06-2X (using either TDA-DFT or TD-DFT) are all very close to those computed with SCS-CC2. The smaller MAD at the TDA-DFT compared to TD-DFT is again ascribed to the former handling better the known triplet instability issue.

ΔE_{ST} and ΔE_{S1T2} show large MAD values when the functional LC- ω PBE is used at both TDA-DFT and TD-DFT levels, in line with the larger MAD for S_1 energy calculations in comparison to both the MADs of T_1 and T_2 excited states energies. For both TDA-DFT and TD-DFT calculations, by tuning ω in the LC- ω *PBE and LC- ω *HPBE functionals, all relative energy differences are now in good agreement with the corresponding ones computed at the SCS-CC2 level, owing to a much better handling of CT states that is reflected in the largely stabilized S_1 . TDA-CAM-B3LYP calculations for ΔE_{ST} , ΔE_{S1T2} and ΔE_{T2T1} are in good agreement with those

using SCS-CC2. In contrast, the MAD values for ΔE_{ST} and ΔE_{S1T2} are much larger using TD-CAM-B3LYP. The similar MAD value for ΔE_{T1T2} at both TD-DFT and TDA-DFT levels suggest that TDA acts similarly on both T_1 and T_2 . Overall, this study reveals the importance for the use of TDA-DFT when employing CAM-B3LYP in order to predict accurately the relative energies of the low-lying excited states.

Based on the calculations of both the absolute and relative energies of the excited states, we can conclude that functionals containing a lower HF-like exchange content such as PBE0 and B3LYP are not appropriate. M06-2X provides a much better description of the excited state energies. The use of CAM-B3LYP within the TDA-DFT approximation is also an appropriate methodology. LC- ω PBE is also not recommended to be used as it offers a poorly described excited state picture, mainly due to the problematic prediction of the S_1 energy. Tuning of ω improves significantly the prediction of S_1 , and both LC- ω^* PBE and LC- ω^* HPBE perform essentially identically. However, our current investigation tends to show that relying on range-separated functionals for which ω is tuned might not be needed to obtain a reliable excited state picture of D-A TADF emitters. Indeed, alternatives such as M06-2X and CAM-B3LYP show comparable accuracies to LC- ω^* PBE and LC- ω^* HPBE and are thus recommended when evaluating the relative energies between excited states. A full summary of MAD, RMSD and σ is found in Table 2, Figure 5 and Figure S5.

Table 2. MAD RMSD and σ of the energy differences between the considered excited states in comparison to SCS-CC2.

	$\Delta E_{ST} / \text{eV}$			$\Delta E_{S1T2} / \text{eV}$			$\Delta E_{T2T1} / \text{eV}$		
	MAD	RMSD	σ	MAD	RMSD	σ	MAD	RMSD	σ
TD - CAM-B3LYP	0.49	0.50	0.12	0.50	0.52	0.15	0.10	0.14	0.09
TDA - CAM-B3LYP	0.17	0.19	0.10	0.19	0.21	0.09	0.05	0.06	0.04

TD - LC-ωPBE	1.32	1.34	0.26	1.37	1.39	0.23	0.13	0.16	0.09
TDA - LC-ωPBE	0.65	0.68	0.19	0.66	0.70	0.23	0.10	0.12	0.07
TD - LC-ω^*PBE	0.12	0.15	0.09	0.13	0.15	0.07	0.07	0.09	0.06
TDA - LC-ω^*PBE	0.12	0.15	0.08	0.11	0.12	0.05	0.10	0.12	0.06
TD - LC-ω^*HPBE	0.12	0.14	0.09	0.13	0.15	0.07	0.07	0.10	0.06
TDA - LC-ω^*HPBE	0.12	0.15	0.08	0.11	0.12	0.05	0.10	0.12	0.06
TD - B3LYP	0.15	0.19	0.12	0.26	0.34	0.21	0.19	0.24	0.15
TDA - B3LYP	0.16	0.20	0.13	0.29	0.39	0.26	0.23	0.29	0.18
TD - PBE0	0.13	0.17	0.11	0.20	0.24	0.13	0.14	0.18	0.12
TDA - PBE0	0.14	0.19	0.12	0.27	0.34	0.21	0.21	0.24	0.13
TD - M06-2X	0.13	0.16	0.10	0.14	0.20	0.14	0.09	0.12	0.07
TDA - M06-2X	0.11	0.15	0.10	0.10	0.12	0.07	0.09	0.12	0.07

3.3. Oscillator strength

The oscillator strength was calculated for each singlet state, (Figure S6 and Table S16). There were consistent predictions across the series of functionals ($MAD < 0.05$); however, σ ranged more widely from 0.04 to 0.12. A slight improvement was found when using TD-DFT compared to TDA-DFT. Despite their poorly described excited states, B3LYP, PBE0 and LC- ω PBE provide the smallest MAD and σ .

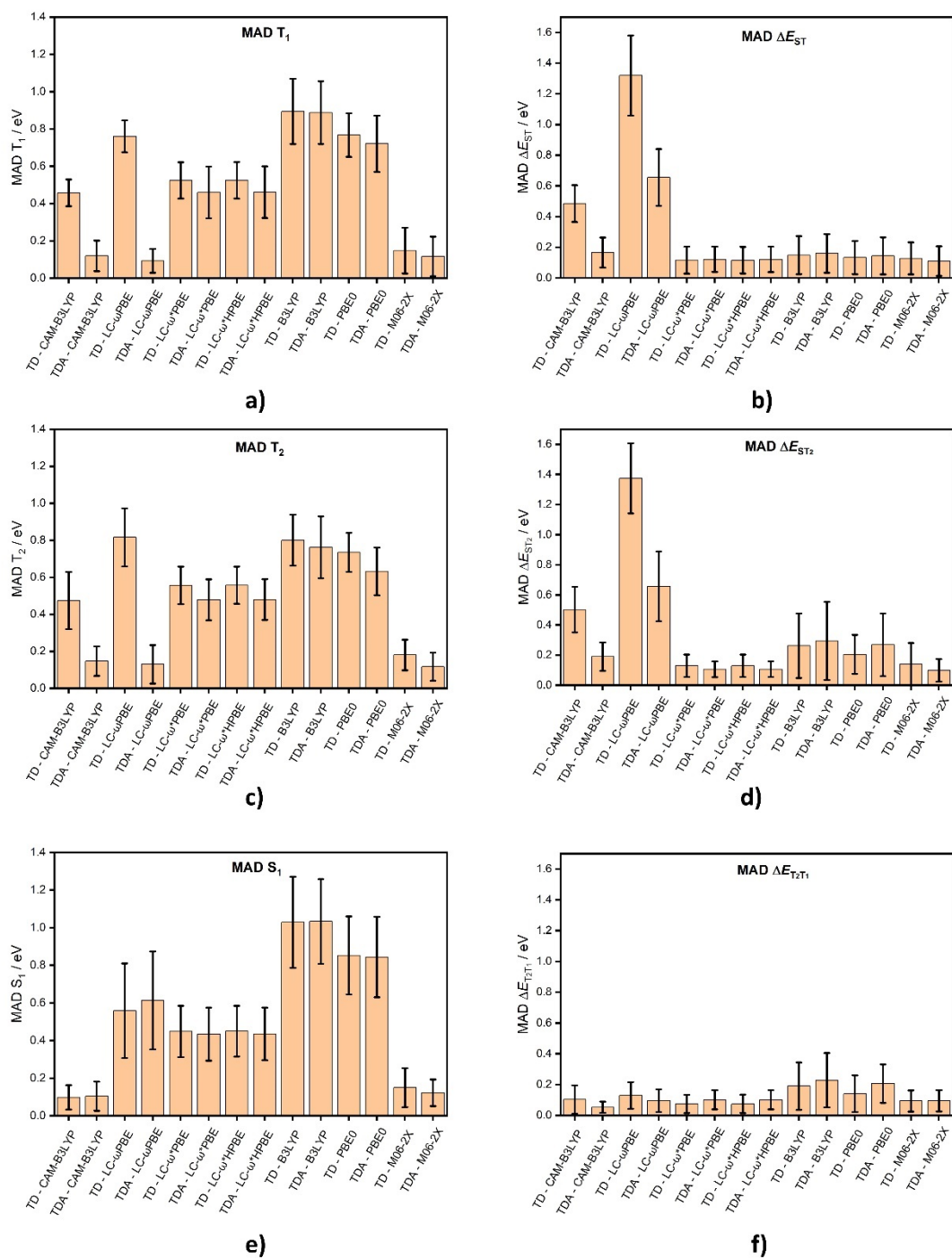


Figure 5. MAD and σ for each functional in comparison to SCS-CC2, where **a)** is T_1 , **b)** ΔE_{ST} , **c)** T_2 , **d)** ΔE_{ST2} , **e)** S_1 , and **f)** ΔE_{T2T1} .

4. Nature of Excited states

The nature of each of the excited states was determined, and a full summary of the ϕ_s , q_{CT} , D_{CT} and S_{+-} metrics is found in the supporting information (ϕ_s values for each emitter, Tables S17

– **S30** and Figures **S7 – S10**; q_{CT} , D_{CT} and S_{+-} values, Tables **S31 – S44** and Figures **S13 – S24**).

We computed the MAD, the RMSD and the standard deviation for the difference in the metrics between TD(A)-DFT and SCS-CC2 for each excited state (S_1 , T_1 and T_2 , Tables **S45 – S47**).

4.1 ϕ_s of DFT functionals

For most emitters, the S_1 state is predicted to be more CT-like compared to T_1 , (lower ϕ_s values) as the exchange interaction increases the spatial confinement of triplet states and thus their LE character. Across all emitters in this study a modest increase in the CT character of the S_1 state is observed when TDA-DFT is used instead of TD-DFT. This is due to the fact that TD-DFT reduces to TDA-DFT when excited states with a large CT character are computed.²⁶ Interestingly, when tracking the nature of the two lowest triplet excited states, we sometimes observe a state inversion depending on the use of either TD-DFT or TDA-DFT. This is particularly evident for **DTPDDA** (Figure **S9d**), where LC- ω *PBE, LC- ω *HPBE and M06-2X at TD-DFT predict a T_1 state with a LE character ($\phi_s > 0.8$), while T_2 remains mainly CT ($\phi_s < 0.4$). However, when TDA-DFT is employed, the T_1 is now a CT state ($\phi_s < 0.4$) with a nature that is very similar to those of T_2 calculated using TD-DFT, while T_2 becomes LE ($\phi_s > 0.8$). These two states are very close in energy to each other (between 0.09 eV and 0.13 eV), with the LE state being pushed above the CT state in TDA-DFT because of its better handling of the triplet instability issue.

The PBE0 and B3LYP functionals display very similar ϕ_s values and tend to predict T_1 and T_2 states to have an increased CT character in comparison to the other functionals. LC- ω PBE appears to be the outlier functional, often resulting in a much larger ϕ_s value. As an example, **PXZ-PXB** has a predicted ϕ_s value for S_1 of > 0.7 while all other DFT functionals predict $\phi_s < 0.3$ (Figure **S10b**). This is evidence of one of the potential issues encountered with long-

range corrected functionals, which tend to destabilize CT states. CAM-B3LYP, LC- ω *PBE, LC- ω *HPBE and M06-2X consistently report very similar ϕ_S values for the S_1 state across the family of emitters in this study, irrespective of whether TD-DFT or TDA-DFT is used. For the triplets, we see a larger spread in T_1 and T_2 ϕ_S values predicted by the CAM-B3LYP, LC- ω *PBE, LC- ω *HPBE and M06-2X functionals compared to S_1 .

4.2 Comparison of the nature of the excited states as predicted using TD(A)-DFT and SCS-CC2

In this section, we embark on a comparison of the nature of the excited states between the different functionals and our reference method SCS-CC2. The nature of the excited state is predicted on the basis of a post-analysis of the difference density. To do so we convert from an attachment-detachment formalism to a difference density picture for all excited states obtained at the TD(A)-DFT level. We compare this picture to the difference density computed at the SCS-CC2 level.

4.2.1 Singlet state

The nature of the S_1 state calculated using DFT and SCS-CC2 methods was compared by computing the q_{CT} , D_{CT} and S_{+-} of S_1 descriptors. While TD(A)-DFT and SCS-CC2 predict a S_1 state with a dominant CT character for essentially all the emitters, one clear outlier exists in terms of **DACT-II**. For this emitter TD(A)-DFT predicts an excited state with largely CT character, while SCS-CC2 predicts that this state contains mainly LE character. Interestingly, the S_2 excited state predicted by TD(A)-DFT is LE-like while SCS-CC2 calculations suggest it is a CT state, which reflects an inversion of S_1 and S_2 (see difference density plots in Figure

6 and Table S25); the energy difference between S_1 and S_2 is small at 0.06 eV using SCS-CC2 while at the TD(A)-DFT, this energy difference is larger, ranging at 0.08 eV to 0.31 eV. Because of this states inversion, the data corresponding to **DACT-II** were removed from the averages on the overall collective data.

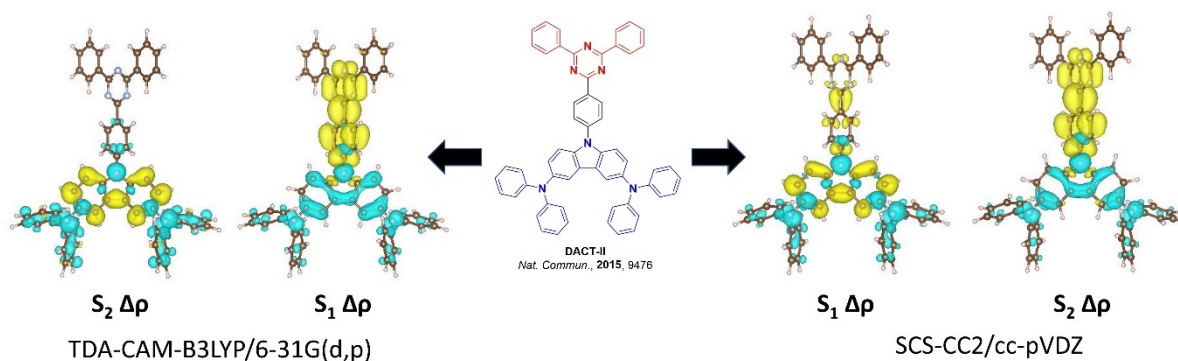


Figure 6. Change in $\Delta\rho$ singlet picture for **DACT-II** between (left) TDA-CAM-B3LYP/6-31G(d,p) and SCS-CC2/cc-pVDZ (right) calculations.

The evaluation of the CT descriptors for the set of compounds confirms the close agreement between CAM-B3LYP and SCS-CC2 for the nature of the S_1 state. The other range-separated functional, LC- ω PBE does not perform as well, with large MAD and σ values for q_{CT} , D_{CT} and S_{+} . (Tables S45 – S47), which are associated with predicted state inversion in **ACRXTN**, **DTCBPy**, **PTZ-DBTO2** and **PXZ-PXB**. When either LC- ω *PBE and LC- ω *HPBE are used, there is close agreement for the description of S_1 and its associated energy with those computed by SCS-CC2. Neither PBE0 nor B3LYP at TD-DFT and TDA-DFT accurately predict the nature of the excited states (Tables S45 – S47). Their overestimation of the CT character explains the heavily stabilized S_1 energy values reported for the absolute energies. Finally, the M06-2X functional provides a similar and equally accurate picture of the nature of S_1 with that of CAM-B3LYP. Based on this analysis, we would encourage the community to use either

CAM-B3LYP, M06-2X, LC- ω *PBE or LC- ω *HPBE to obtain accurate predictions of the nature and energy of the S_1 state.

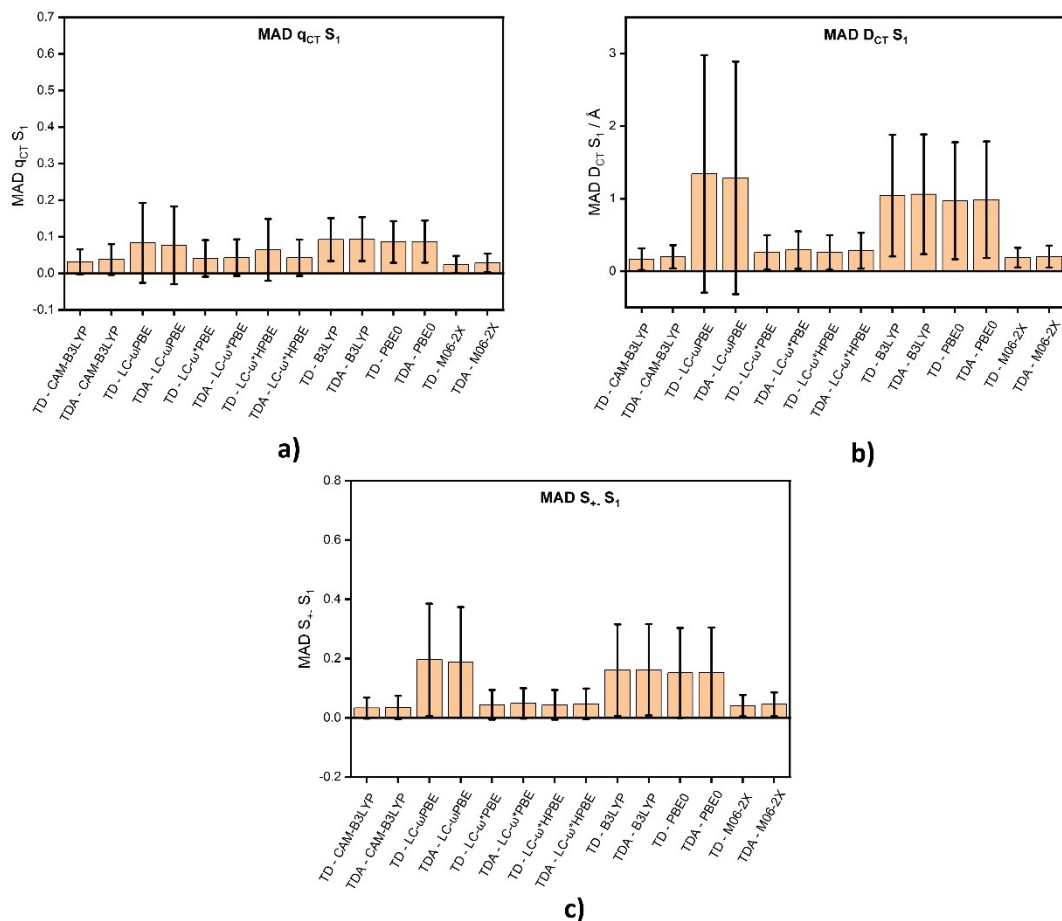


Figure 7. MAD data for the S_1 state nature between TD(A)-DFT and SCS-CC2 calculations, where **a)** is q_{CT} , **b)** is D_{CT} and **c)** is S_+ .

4.2.2 Triplet states

We next discuss the data associated with the prediction of the triplet state character. The nature of T_1 as computed at TDA-CAM-B3LYP is closer to the one predicted with SCS-CC2 than at the TD-CAM-B3LYP level (see CT metrics reported in Tables S45 - S47). However, the opposite is observed for T_2 , wherein the MAD values of the CT descriptors increase when

moving from TDA-DFT to TD-DFT. Overall, it should be noted that the T_1 and T_2 MAD values are significantly larger than the respective S_1 observations.

LC- ω PBE does a poor job in predicting the nature of both T_1 and T_2 ; still, the use of TDA improved the MAD for each excited state descriptor compared to TD-DFT. Unfortunately, neither the use of LC- ω^* PBE nor LC- ω^* HPBE produced a more accurate descriptor of the triplet state character (MAD values similar to those of LC- ω PBE) despite there being a significant improvement in the quality of the energy prediction.

As for S_1 , both B3LYP and PBE0 produce erroneous T_1 and T_2 assignments as the CT character of these states is overestimated. Inclusion of greater HF like contribution within M06-2X improves the triplet description, though the discrepancy compared to SCS-CC2 is much larger than that observed for the description of the S_1 state.

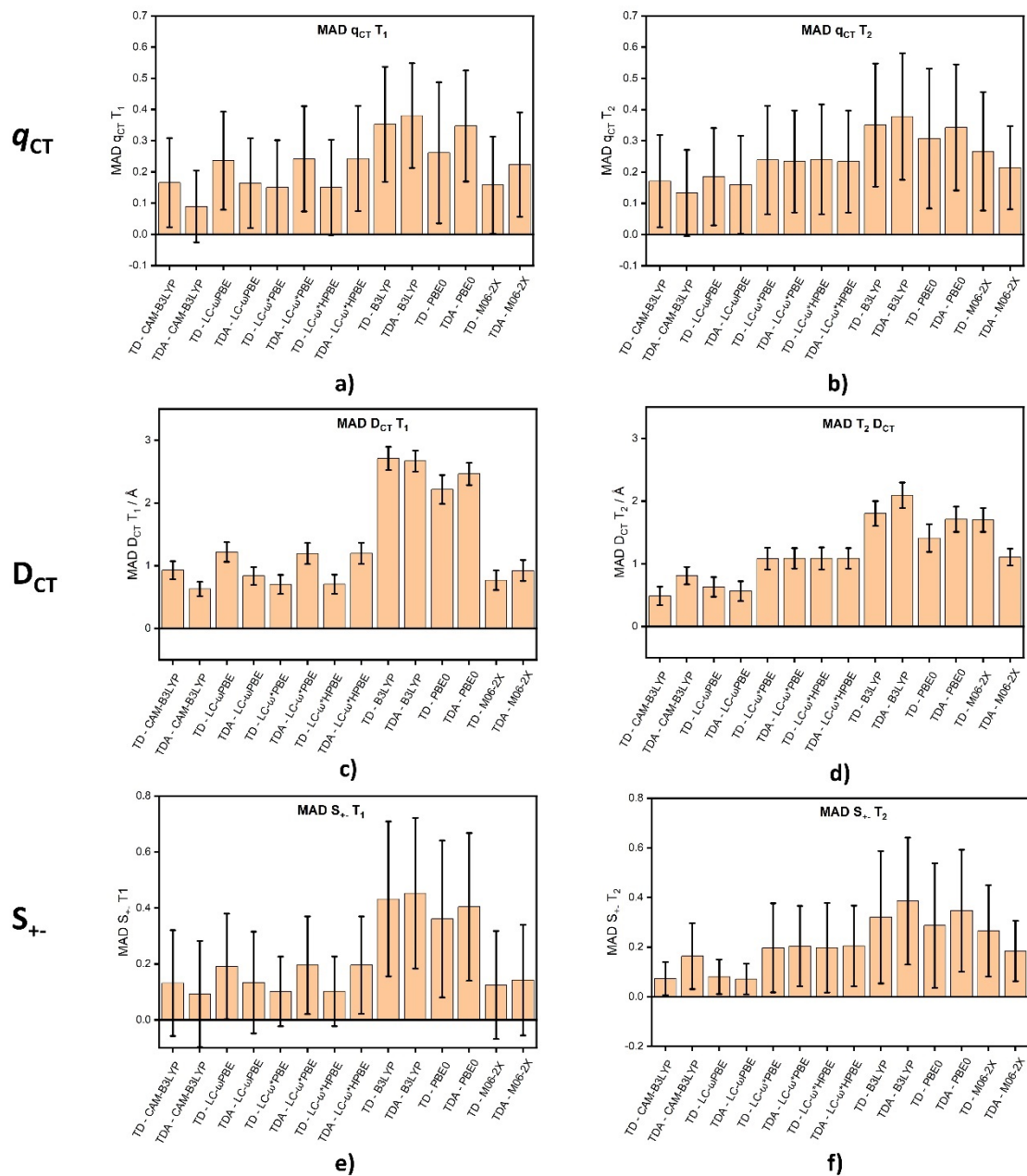


Figure 8. MAD data for the T_1 (left) and the T_2 (right) states nature between TD(A)-DFT and SCS-CC2 calculations, where **a)** and **b)** are q_{CT} , **c)** and **d)** are D_{CT} and **e)** and **f)** are S_{+-} .

5. Excited states optimization

We further complement this study by optimizing the S_1 and T_1 excited states and investigate the change in ΔE_{ST} as well as the nature of the latter excited states between vertical and adiabatic excitations as previously highlighted.²²⁻²³ We therefore next selected a subset of the

materials (**2CzPN**, **4CzBN**, **ACRPOB**, **DMAC-DPS**, **DTCBPy** and **PXZ-PXB**) reported in Figure 4, because of their relatively wide range of excited state natures (*vide supra.*). In this section, we restricted the functionals investigated to CAM-B3LYP, M06-2X and PBE0 considering the 6-31G(d,p) basis set within the TDA and compared these results to SCS-CC2 excited states energies computed on the TDA-DFT S_1 and T_1 geometries.

5.1. Excited-state energies

As expected, there is a stabilisation in both the S_1 and T_1 energies when these excited states are optimized for each material at each functional. An increase in ΔE_{ST} moving from vertical to adiabatic excitation is observed using CAM-B3LYP functional as a consequence of a largely stabilized T_1 . CAM-B3LYP is known to cure for the large destabilization of CT states observed with functionals with low Hartree-Fock exchange such as B3LYP and PBE0 and therefore leads to a relative stabilization of LE-like excited states.⁵² Especially, **4CzBN** and **DMAC-DPS** show the most prominent changes, with ΔE_{ST} moving from 0.45 eV and 0.12 eV using vertical excitation, increasing to 1.10 eV and 0.66 eV considering optimized S_1 and T_1 geometries, respectively. The SCS-CC2 calculated ΔE_{ST} follows also the trend predicted by the different DFT functionals (either an increase or a decrease in ΔE_{ST}) but seems to be less sensitive on the TDA-DFT optimized geometries. Still, SCS-CC2 estimates of ΔE_{ST} for **4CzBN** and **DMAC-DPS** are also very large (**4CzBN** and **DMAC-DPS** SCS-CC2 ΔE_{ST} are 0.96 eV and 0.53 eV, respectively) based on the CAM-B3LYP excited states geometries while PBE0 and M06-2X S_1 and T_1 excited states energies lead also to an increase but to a smaller extent. Abnormal negative ΔE_{ST} are observed considering the optimized S_1 and T_1 excited states PBE0 geometries (**2CzPN** and **4CzPN** have ΔE_{ST} of -0.03 eV and -0.06 eV, respectively). Most other examples undergo a decreased ΔE_{ST} moving from vertical to adiabatic excitation, with S_1 stabilisation key. For M06-2X, increased ΔE_{ST} moving from vertical to adiabatic is apparent for most examples, however it is less severe compared to CAM-B3LYP. Moreover, the ΔE_{ST} 's

computed for the set of selected molecules remain in a range where these compounds would be TADF-active in line with the experiments so that M06-2X appears as the recommended functional when dealing with excited state optimization. The oscillator strength of the S_1 excited state of the different emitters is not dramatically affected whether it is computed from the ground or the S_1 excited state geometries or by varying the functional.

5.2. Excited-state natures

We calculated the nature of the optimized S_1 and T_1 states considering the metrics defined in section 2.1 (*vide supra.*), comparing the changes between vertical and adiabatic excitations (Table S54 – S65). For the S_1 excited state, moving from vertical to adiabatic excitation there is a minimal change in the CT content for the compounds displaying excited states with a large CT content, **PXZ-PXB**, **DTCBPy**, **DMAC-DPS** and **ACRPOB** irrespective of functionals as exemplified by the ϕ_s calculations (see Tables S56-S59). For **2CzPN** and **4CzBN**, the nature of the S_1 state obtained from vertical excitation from the ground state leads to a mixed CT/LE ($\phi_s = 0.40 - 0.50$ for each at each functional) state. The optimization of S_1 for these two compounds leads to an increased CT content for most functionals and a subsequent decrease in ϕ_s resulting in a CT-like excited state.

As for vertical excitation calculations, a large disparity in the nature of the T_1 state is observed. The CAM-B3LP functional predicts a minimal change in the nature comparing vertical to adiabatic excitation, with a dominantly LE character of each compound maintained. The PBE0 functional overall leads to a T_1 state with a dominant CT character in line with the previous vertical excitation calculations. **2CzPN** is the only exception, where a higher lying CT triplet ($\phi_s = 0.30$) is swapped with the mixed CT-LE ($\phi_s = 0.67$). Similarly, T_1 optimization with the M06-2X functional leads to a state inversion for **4CzBN**, **ACRPOB** and **DMAC-DPS** since a higher lying LE triplet is now stabilized below the previously more CT state. Finally, SCS-

CC2 calculations were performed on top of the TDA-DFT optimized T_1 geometries showing a similar trend in the T_1 nature as obtained with the different functionals.

6. Conclusions

We have compared the results of DFT calculations across a series of commonly used functional to predictions made using SCS-CC2 of (i) vertical excitation energies, (ii) vertical excitation energy differences and (iii) nature of excited states for a series of fourteen TADF emitters. The objective of our study was to determine the best choice of functional for modelling the optoelectronic properties of donor-acceptor TADF compounds. We observed that TDA-DFT calculations provided a more accurate prediction of the vertical excitation energies compared to TD-DFT, as has been previously documented.^{26, 28} Both TDA-M06-2X and TDA-CAM-B3LYP calculations provide very good agreement for S_1 , T_1 and T_2 ; TDA-LC- ω PBE calculations produce reasonably accurate T_1 and T_2 energies, but consistently overestimate the S_1 energy. B3LYP, PBE0 and the ω -tuned functionals consistently underestimate triplet and singlet state energies, resulting in large deviations from the SCS-CC2 calculations. When considering excited state energy gaps, TDA-LC- ω PBE and TD-DFT-LC- ω PBE calculations produce large deviations in both ΔE_{ST} and ΔE_{ST2} , the result of the much larger MAD for S_1 than for T_1 and T_2 . ΔE_{T2T1} is much better reproduced for most functionals in comparison with ΔE_{ST} and ΔE_{ST2} . However, PBE0 and B3LYP show comparable MADs but larger standard deviations when evaluating ΔE_{T2T1} questioning their reliability in predicting this parameter. Of the functionals evaluated, TDA-M06-2X and TDA-CAM-B3LYP offer the most accurate predictions, evidenced by their low MADs for ΔE_{ST} , ΔE_{ST2} and ΔE_{T2T1} ; the MAD values increased for the analogous TD-DFT calculations as here the triplet states are overstabilized. Finally, we investigated the nature of the excited states, computing the q_{CT} , D_{CT} and S_{+-} CT descriptors for T_1 , T_2 and S_1 excited states. Apart from **DACT-II**, the nature of the S_1 state is

in good agreement with SCS-CC2 when considering the CAM-B3LYP and the M06-2X functionals for both TD-DFT or TDA-DFT calculations. By contrast, B3LYP and PBE0 perform the worst with S_1 states predicted to have a larger CT character. When tuning the range separation parameter, LC- ω *PBE and LC- ω *HPBE perform better compared to the original LC- ω PBE functional and with a similar accuracy as for the CAM-B3LYP and M06-2X functionals. Overall, we found that regardless of the functional the excited state description is not as well reproduced for triplets as it is for singlets, which is reflected in the larger MAD for every CT descriptor. Of the functionals assessed that did not require parameter tuning, both CAM-B3LYP and M06-2X provide the most accurate predictions of the character of the low-lying excited states. We therefore encourage the community to adopt either of these two functionals in combination with TDA-DFT calculations in order to obtain the most accurate modelling for TADF materials, however direct assignment of T_1 and T_2 natures must be done with caution for the vertical excited states. We carried out S_1 and T_1 excited states optimization with the CAM-B3LYP, PBE0 and M06-2X functionals. CAM-B3LYP reported for some compounds very large ΔE_{ST} which would not allow them to be TADF-active while PBE0 predicted unrealistic negative ΔE_{ST} for few emitters. M06-2X provides intermediate ΔE_{ST} values which are not drastically different than ΔE_{ST} obtained from vertical excitation. While the prediction of the nature of the S_1 state with the different functionals is overall the same, there is a larger disparity for the T_1 state. While CAM-B3LYP and PBE0 suggested a more LE and CT character, respectively, M06-2X leads to a nature intermediate between these two functionals. Based on these findings on a modest sample, we would again urge caution when dealing with triplets with different functionals producing contrasting results. In complement, we performed SCS-CC2 calculations on top of the TDA-DFT geometries obtained with the different functionals and observed a large dependence of both the ΔE_{ST} and the nature on the optimized geometries. However, the effect of excited states geometry optimization should be

investigated more thoroughly and would require an independent study going beyond the object of this work.

Supporting Information

Photophysical and device data of studied emitters and supplementary computational data of all studied emitters along with coordinates.

Acknowledgments

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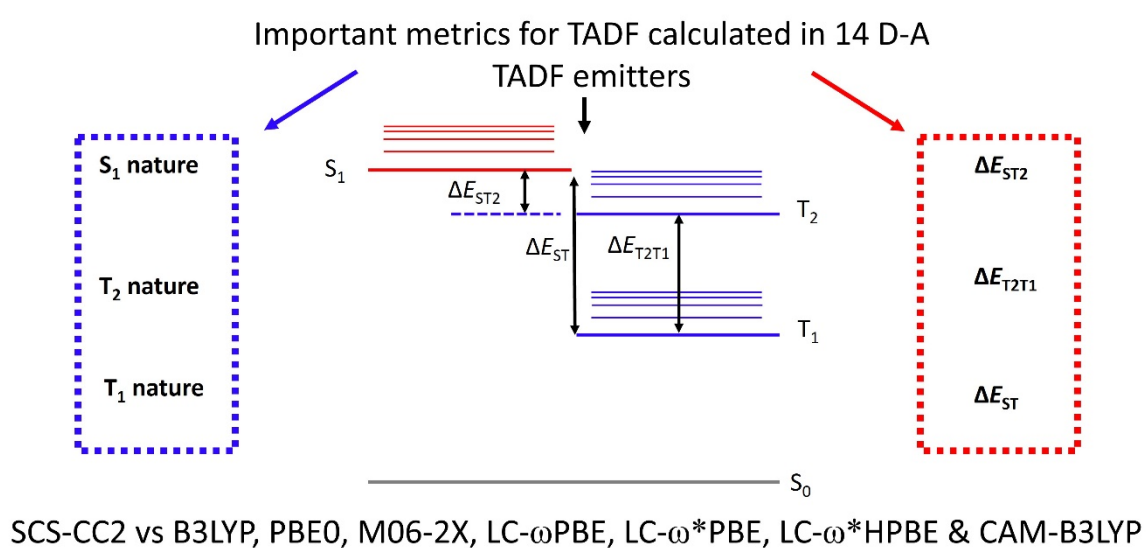
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TOC



M06-2X and CAM-B3LYP offer most consistent results!